

Temporal and Spatial Scales of Terrestrially-derived Particulate and Dissolved Materials in the Penobscot River System: Quantifying Conserved and Non-conserved Optical Properties and Transformations within the Estuary

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LONG-TERM GOALS

Coastal waters represent the commingling of offshore marine and terrestrial surface source waters and therefore are naturally complex and variable. Our long term goal is to establish observational and modeling approaches to predict sources and scales of variability in the source waters, particularly those related to land use activities in upstream watersheds, from observations and measurements in the coastal waters.

OBJECTIVES

Hydrologic optics provides an approach to characterizing physical and biogeochemical processes in aquatic systems over a range of time and space scales. The linkage between observations of the inherent optical properties (IOPs; absorption, scattering and fluorescence) and the geophysical properties lie in the establishment of robust optical proxies and the quantification of the temporal and spatial scales over which these proxies remain conservative in their properties. Our objectives are to identify and quantify specific optical and chemical characteristics of the colored particulate and dissolved fractions originating in the Penobscot River system that are associated with defined land use activities (land use proxies), and to determine the scales of variability over which these proxies can be detected both temporally (i.e. seasonal and episodic events) and spatially (from the source into coastal waters).

APPROACH

Our approach combines high resolution temporal and spatial hydrographic and optical observations from moored, surface underway and undulating platforms with chemical characterization of the organic and inorganic, particulate and dissolved carbon and nitrogen pools that originate in the sub-watershed drainage basins of the Penobscot River System and flow through Penobscot Bay estuary into

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the coastal waters of the Gulf of Maine. Our approach is to (1) identify optical proxies for biogeochemical parameters, including quantifying the time and space scales of conservative behavior; (2) apply these proxies to high-resolution time and space optical observations to compute concentration and flux of river borne material into the estuary and coastal systems; (3) compare models for conserved behavior with observations to identify zones and times of non-conserved behavior; (4) elucidate transformation processes at these locations/times; (5) quantify impacts of land use on the biogeochemical properties of the coastal ocean with the goal to predict responses to climate induced hydrologic forcing.

WORK COMPLETED

Optical Proxies for Biogeochemical Parameters are quantified from paired optical observations and biogeochemical analyses collected on monthly watershed sampling trips, semi-annual estuary surveys and occasional buoy operations trips. To date we have completed 43 samplings of up to 22 stations within the Penobscot River Watershed, 6 complete surveys of between 25 and 45 stations within the Penobscot Bay Estuary, and collected samples associated with buoy deployment/recovery activities in the Gulf of Maine coastal waters (Figure 1).

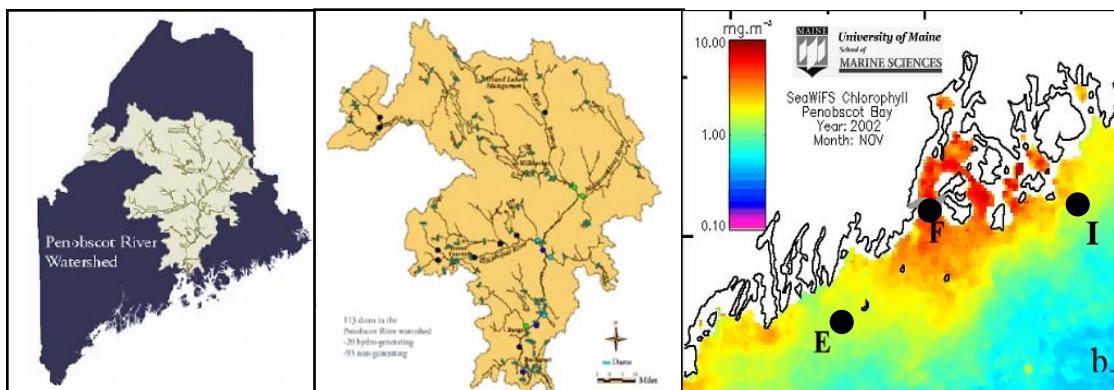


Figure 1. Sampling Program for Penobscot Watershed and coastal waters. A. Map of the state of Maine with the Penobscot River and Watershed indicated. B. Detail of Watershed showing location of monthly sampling stations (green) and moored triplet sensors (blue). C. SeaWiFS false color image of November chlorophyll concentration showing high values of apparent chlorophyll induced by high CDOM flowing out of the Penobscot River and Bay and into the waters of the Eastern Maine Coastal Current. The locations of GoMOOS Buoys E, F and I are indicated by black symbols.

Each station/site consists of paired optical observations samples (e.g. backscattering and CDOM and Chl fluorescence) and biogeochemical and optical analysis of discrete water samples (e.g. particulate and dissolved spectrophotometric analysis, excitation emission matrices, extracted pigments, CHN, TSS, DOC, TDN, nutrients, pH, temperature, conductivity. We have completed all optical and biogeochemical analyses of these samples, have quantified the spatial and temporal patterns within the river and estuary, and have quantified optical proxies for the major particulate and dissolved properties.

High temporal resolution of optical proxies for biogeochemical parameters are obtained via moored optical sensors within the Penobscot River to quantify export from the terrestrial environment (e.g. triplet/BBFL2 sensors), and in the Penobscot Bay estuary (e.g. Penobscot LOBO and GoMOOS buoy

F) as well as in the coastal waters upstream and downstream of Penobscot Bay (e.g. GoMOOS buoys E and I). We have successfully deployed and recovered 17 in situ triplet sensors (backscattering and CDOM and Chl fluorescence) at 4 locations within the Penobscot River. The Penobscot LOBO mooring, which consists of both optical and biogeochemical sensors, was successfully deployed 22 June 2008 and serviced in August 2008. GoMOOS buoys E, F, and I have been providing hourly optical observations since July 2001 (E and I) and since 2005 (buoy F). We have completed the data analysis of the river moorings and are finishing the analyses of the applicable buoy observations.

Modeling conserved and non-conserved behavior of river borne material into the estuary and coastal waters starts with the pattern of export from the river. By combining the optical proxies derived from discrete observations, moored observations within the river and daily USGS discharge data, a 4-1/2 year time series of exported matter has been computed. Based upon some limited analysis of 7 months of observations in 2005, we concluded that significant loss of dissolved matter was occurring in the estuary. We are now in the process of expanding this analysis to the entire time series to look for seasonal and interannual variations from the initial analysis. In addition, we have identified the location within the estuary where the majority of the non-conserved transformations appear to be occurring and have placed a high resolution optical and biogeochemical buoy at that location to elucidate the transformation processes on highly resolved scales.

Two major sinks of organic matter in the estuary appear to be photo-oxidation and particle flocculation and sinking. With regards to photo-oxidation of CDOM in the near surface waters, we observe daily fluctuations in in situ CDOM fluorescence of up to 30%. During this year's summer survey, we performed an on-deck photo-oxidation experiment to quantify the loss of fluorescence, absorption, and DOC in concert with the reduction of both dissolved oxygen and pH (due to the increase in CO₂ from the organic matter oxidation). We observed this phenomenon both in situ and in our incubation. We are in the process of quantifying the losses and will use the rates in our model of non-conservative processes. To elucidate the second loss term, we have deployed a Sequoia LISST particle size analyzer on the LOBO mooring. The goal of these observations is to quantify the rates of change of non-conservative particle formation and CDOM loss the rates of which will be included in our model of non-conservative processes. We have just recovered the data from the LISST from the first deployment and are in the process of analyzing the data set.

RESULTS

River Processes - The Penobscot River Watershed

Optical Proxies, Phytoplankton and Nutrients: We have made great progress in our quantification of Optical Proxies for Biogeochemical properties since the beginning of this program. The weakest proxy has been that for chlorophyll, a surprising result considering the use of in situ fluorometry. Temporal and spatial analysis pointed in three directions, (1) fluorometric chlorophyll significantly overestimated extracted chlorophyll at stations characterized by drainage of freshwater wetlands and high CDOM concentrations in the tributaries; (2) fluorometric chlorophyll significantly underestimate extracted chlorophyll during large cyanobacterial blooms; (3) great care has to be taken to account for diel variations associated with non-photochemical quenching of fluorescence (i.e. the timing of discrete observations has to be corrected for time of day and solar insolation).

We have since determined that all of our in situ chlorophyll fluorometers must be calibrated against in situ CDOM concentrations to determine the offset caused by CDOM fluorescence induced by the Chl excitation LED leaking into the Chl fluorescence channel. This correction works best when in situ

paired observations of both Chl and CDOM fluorescence are made (such as with a BBFL2) but can also be applied if a CDOM absorption measurement is made (spectrophotometrically or with a filtered ac9) and the CDOM fluorescence quantum yield is known (this turns out to be remarkably constant for the appropriate wavelengths, Belzile et al. 2006). The exact correction scheme is outlined in Proctor (2008) and Proctor and Roesler (MS thesis in manuscript form for submission to L&O methods). With regards to underestimation of cyanobacterial blooms, Proctor (2008) and Proctor and Roesler (manuscript) determined the species-specific calibrations for fluorometers and found that the standard Chl excitation LED (470 nm) yields very weak response in the presence of phycobilipigment-containing phytoplankton. By using a three-LED version of the Chl fluorometer (3X1M) they concluded that the variable pigment-based spectral response to the 3 excitations was sufficient to identify major pigment-based taxonomic groups (a pigment-based classification of Phytoplankton Functional Type, PFT) and this information allowed the PFT-specific calibration slope to be applied to the fluorometer for more accurate estimation of chlorophyll concentration. However, this requires the 3-wavelength version, which is not quite available commercially.

The results are that we made significant improvements to the algal optical proxy (Figure 2A) and can now evaluate the dynamics of phytoplankton in the Penobscot River: (1) algal blooms generally occur in July-august and rarely exceed 5 $\mu\text{g/l}$ chlorophyll (Figure 2B); (2) the exception is the occurrence of cyanobacterial blooms that are in response to discharge of high concentrations ($>5\mu\text{M}$) of phosphate from local mills; (3) the river is not a major source of inorganic nutrients to the estuary with nitrate (phosphate) rarely exceeding 10 μM (1 μM) in the late autumn to late winter and less than 5 μM (0.2 μM) in the spring and summer. Silicate, on the other hand displays summertime maximal values exceeding 80 μM , with wintertime lows of $<40\mu\text{M}$, always a source to the downstream marine waters (Figure 2C). Highest nutrient concentrations occur farthest upstream with concentrations decreasing with phytoplankton usage as a function of distance down river; (4) algal concentration is a robust predictor of the particulate organic C:N ratio (by weight) which varies from ~6 during algal blooms to ~15 when algal concentrations are minimal. Thus the river acts more as a source of dissolved inorganic Si and phytoplankton particulate organic N and P (rather than the inorganic dissolved NO_3 and PO_4);

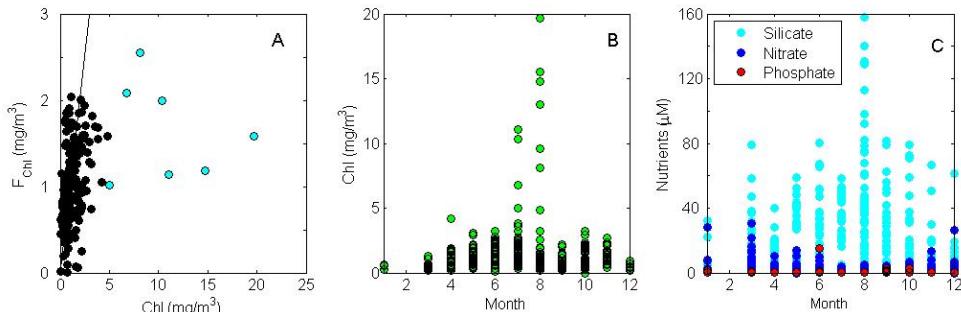


Figure 2. Phytoplankton in Penobscot River. A. Phytoplankton optical proxy of in situ Chl fluorescence as a function of extracted chlorophyll concentration, cyanobacterial bloom stations in cyan. Line is 1:1 line. B. Monthly distribution of phytoplankton blooms as indicated by chlorophyll concentration for all stations. C. Monthly distribution of inorganic nutrients. Monthly samples from up to 22 stations, 2004-2008.

Optical Proxies and Suspended Particles: The total particle load as measured by concentration, total suspended particles (TSS), and composition, particulate organic carbon (POC), can be represented by a particle backscattering proxy (Figure 3). Although more closely related to TSS (data not shown), the backscattering proxy for POC is dependent upon discharge and hence time of year (Figure 3A) as shown by the steepest slopes during the spring (Jan-June) when discharge is the highest and carbon

content the lowest, compared to mid summer when the carbon content of the particles is highest and related to algal blooms. The spectral slope of the non-algal absorption coefficient is similarly dependent upon carbon content which steeper slopes associated with carbon-poor particles (Figure 3B). Finally the total export of particulate carbon increases along the river, although a similar relationships not observed in total particle load, thus the particles are becoming more organic during transport either due to primary production or due to adsorption of organic coating onto inorganic particles (Figure 3C).

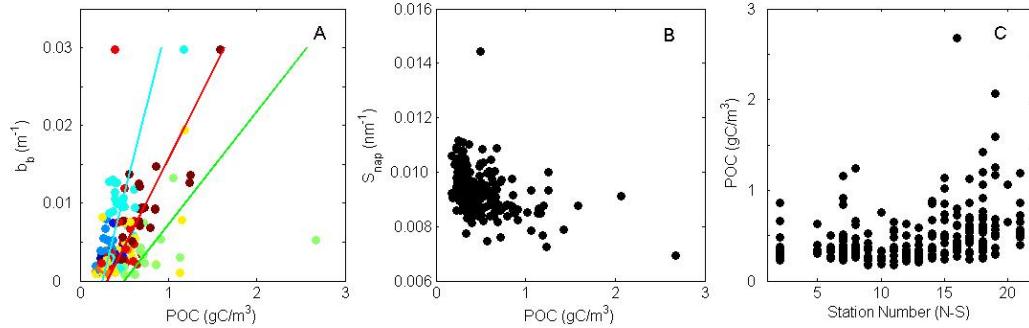


Figure 3. Particles in the Penobscot River. A. Dependence of the particle backscattering proxy for POC as a function of season (which convolves both discharge/resuspension and biological production). B. Spectral slope of the non-algal particle absorption as a function of organic carbon concentration. C. Dependence of POC concentration as a function of distance down river.

Optical Proxies and Dissolved Organic Matter: (Note that the DOC analysis was performed as part of a NASA-sponsored program by Dr. George Aiken, USGS Boulder) The dissolved organic matter fluorescence is a robust proxy for DOC, particularly for stations that are not characterized by freshwater wetlands (Figure 4A). These wetland stations exhibit a lower fluorescence quantum yield because of the exact nature of the organic matter. The CDOM absorption coefficient is an even more robust proxy for DOC (Figure 4B), independent of station or season. The specific absorption of the dissolved matter in the river (i.e. SUVA = $a(370)/\text{DOC}$), an indicator of DOC composition, does vary and is well predicted by the CDOM absorption spectral slope, S_{CDOM} (Figure 4C).

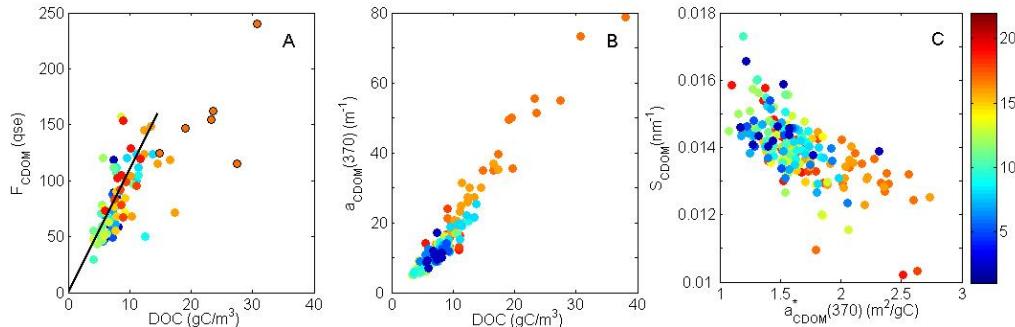


Figure 4. Dissolved matter proxies as a function of station (upriver to downriver). A. Fluorescence and B. absorption proxies for DOC as a function of station (orange symbols with black edges are associated with stations draining wetlands and are not included in regression in A). C. The spectral slope optical proxy as a function of the carbon-specific UV absorption coefficient (a.k.a. SUVA).

Estimating Carbon Flux in the River: Once the proxy relationships established above are applied to the in situ optical observations, the time course of organic carbon export for each component is

quantified (Figure 5). On average phytoplankton are responsible for <1% of the exported organic carbon, non-algal particles represent ~8% of the export, while DOC represents ~92% of the exported carbon, $\sim 2 \times 10^5$ kg C/d on average with peaks exceeding 10×10^5 kg C/d.

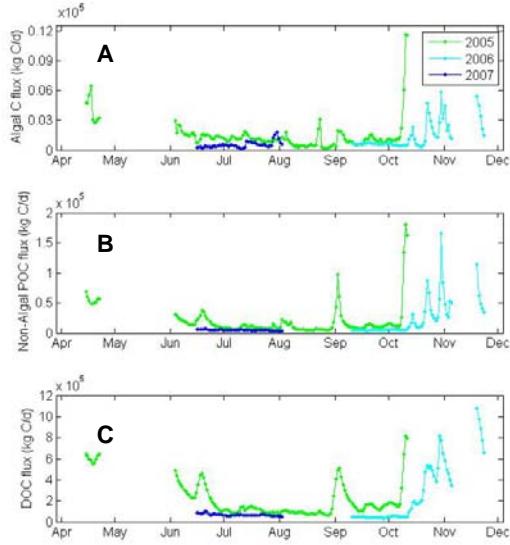


Figure 5. Time series of *A. algal*, *B. non-algal* particles, and *C. dissolved organic carbon* export estimated from moored triplet observations of F_{Chl} , b_{bp} , and F_{CDOM} , respectively, converted to Chl , POC and DOC using the proxies derived above (Chl is further converted to algal carbon using published values). Export is computed from the product of the discharge (m^3/d) and carbon concentration ($kg\ C/m^3$).

Given the dominance by the DOC fraction, further examination of the relationship of DOC concentration and discharge revealed, contrary to expectation, that DOC concentration in the river was linearly related to the discharge rate (Figure 6A). It does not appear to dilute our as runoff increases. This has the multiplicative effect on export as the export of DOC is

proportion to the square of the discharge (Figure 6B). However, what the moored observations have yielded is a statistically significant 3-day lag of DOC concentration behind discharge ($r^2=0.81$). Thus, daily discharge, for which there is a hundred year record, is used to predict daily F_{CDOM} via the relationship in Figure 6A, and F_{CDOM} is used to predict high resolution estimates of DOC via the optical proxy (Figure 4A).

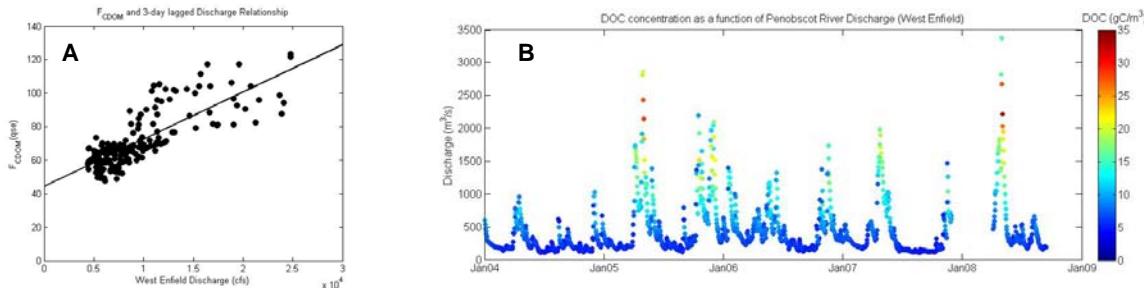


Figure 6. A. Relationship between F_{CDOM} observed at with a moored BBFL2 at the Eddington and the daily discharge observations from the USGS gage at West Enfield (there is no statistically significant lag between West Enfield and Eddington gages, the West Enfield gage is used here because it has a longer time series). B. Time series since January 2004 of daily discharge at West Enfield, DOC concentrations indicated by symbol color.

The organic carbon export for the Penobscot River can then be estimated from the product of discharge and DOC concentration, noting that the total particulate contribution can represent up to 8% of the total organic carbon (Figure 7). The non-algal POC is significantly correlated with DOC due to the influence of high flow on particle resuspension.

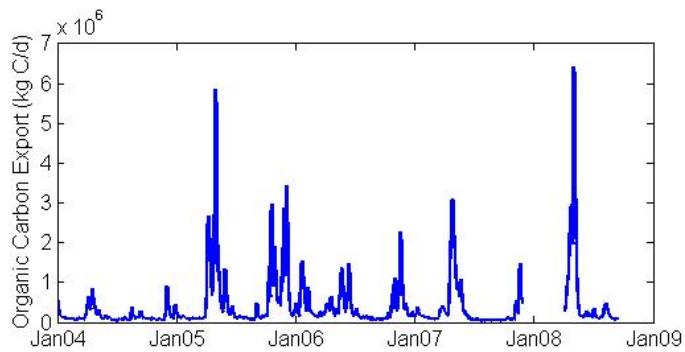


Figure 7. Daily export of organic carbon in the Penobscot River 2004- 2008 (present). Springtime export exceeds autumn export. Significant year-to-year variations occur (e.g. 2004 vs. 2005).

The time series demonstrates the importance of both the spring freshet and the autumn precipitation seasons. Our sampling period has covered both a drought year (2004) followed by the wettest year in a century (2005) and the second wettest (2008). Predictions for this region, with regards to climate effects on hydrology suggest that the norm will be hotter drier summers with early more intense springtime melting and precipitation and later and more intense autumn precipitation. This suggests that the export of carbon will similarly intensify which will have impacts not only on export but also on ecosystems downstream dependent upon the river materials.

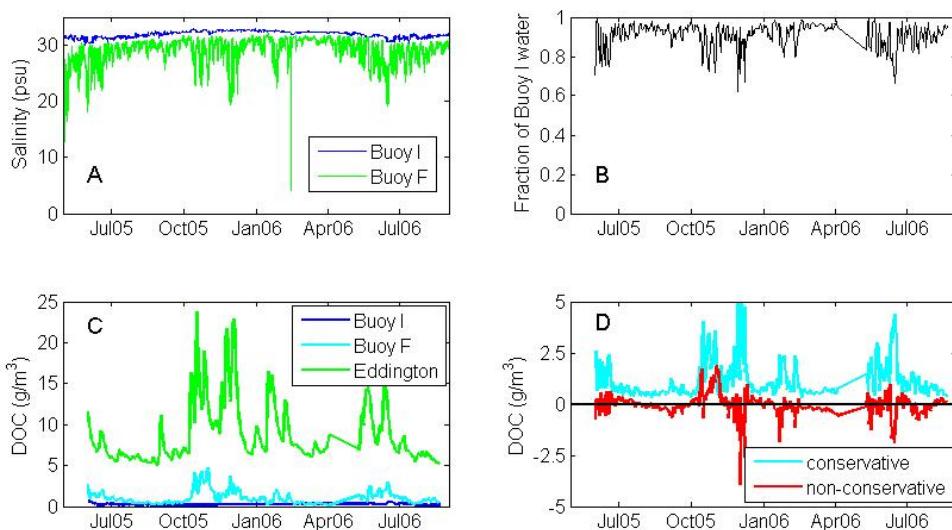


Figure 8. Example of modeling conservative and non-conservative DOC processes in Penobscot Bay. A. Salinity observed at Buoys F and I (lower Penobscot Bay and upstream Eastern Maine Coastal Current, respectively). B. Fraction of marine water (Buoy I) observed at Buoy F based upon conservative mixing of salinity. C. Observed DOC time series (from moored F_{CDOM} and DOC proxy) in the Penobscot River (Eddington), Penobscot Bay (Buoy F) and coastal waters (Buoy I). D. Modeled DOC at buoy F based upon conservative mixing in the estuary (cyan) and non-conservative DOC (Modeled - Observed; red).

Estuarine Processes- Penobscot Bay

Once DOC enters the estuary it is subject to a range of non-conservative processes. To investigate the magnitude of these processes, we quantified the conservative transport of F_{CDOM} (DOC) from the lower river (Eddington site) to the lower bay (GoMOOS buoy F off Rockland). It takes a parcel of water approximately 4 days to be transported downstream from Eddington to Buoy F (based upon lagged cross correlation analysis). Using the observed salinity values at F and I (Figure 8A), the daily conservative mixing fraction of Buoy I water ($F_{BI}(t)$) was computed (Figure 8B):

$$F_{BI}(t) = S_{BF}(t) / S_{BI}(t)$$

and therefore the fraction of fresh source water, from Eddington, was:

$$F_{Edd}(t) = 1 - F_{BI}(t).$$

The observed time course of DOC at Eddington (green), buoy F (cyan) and buoy I (blue) is shown in Figure 8C. While the conserved DOC, DOC_{BFmod} (Figure 8D, cyan), was predicted from the relative proportions of the freshwater and marine DOC endmembers:

$$DOC_{BFmod}(t) (gC/l) = F_{Edd}(t) * DOC_{Edd}(t) + F_{BI}(t) * DOC_{BI}(t)$$

The difference between observed and predicted conserved DOC is the non-conserved DOC (Figure 8D, red). The only time there is significant non-conserved behavior is during the high flow periods, and with one exception, the loss in DOC can exceed 40%. This observation is contrary to our working hypothesis that higher discharge rates, although associated with higher DOC, would lead to lower non-conservative properties because of the rapid timescales of transport through the estuary. However, statistically, the greatest loss of DOC occurs during these periods.

Coastal Water Processes- Gulf of Maine

The impact of the Penobscot River on the coastal waters of the Gulf of Maine is not so much with respect to nitrogen and phosphorus, as these nutrients are in relatively low concentrations and are utilized by river algal populations during the growing period, but more to the very high concentrations of CDOM and DOC. The quality of the DOC has been characterized by our colleague George Aiken (USGS, Boulder). The tributaries that are found in the lower river contribute a very aromatic and labile carbon, which is likely why we find such high losses of readily utilized DOC in the estuary. We are currently investigating the flux of this matter into the coastal waters where it might serve to stimulate productivity.

The CDOM transport from the Penobscot River and its impact on watercolor are apparent to anyone who has seen the clear green waters of the Gulf of Maine. The impacts are remote sensing of ocean color are significant. Figure 1C shows a November "bloom" of phytoplankton in Penobscot Bay and surrounding waters that is certainly due to the high flux of CDOM. The reason for this is that the NASA ocean color algorithms for chlorophyll are driven by the absorption ratios for phytoplankton (mostly due to chlorophyll) in the blue and green regions of the spectrum. However, CDOM absorbs very similarly to phytoplankton at the ocean color sensor channels (Figure 9A), and thus any algorithm based upon radiance ratios will not be able to distinguish CDOM from chlorophyll. In fact a comparison of chlorophyll observed at GoMOOS buoy E (downstream of Penobscot Bay, Figure 1C) and MODIS-derived chlorophyll demonstrates the impact of CDOM on chlorophyll retrieval (Figure 9B). These effects tend to be worse in the early spring just prior to the spring bloom and in the late autumn after the fall bloom, when CDOM inputs are maximal in response to the spring freshet and fall precipitation periods. The impact is that ocean color-based analysis of phytoplankton dynamics tends to overestimate the duration of the blooms.

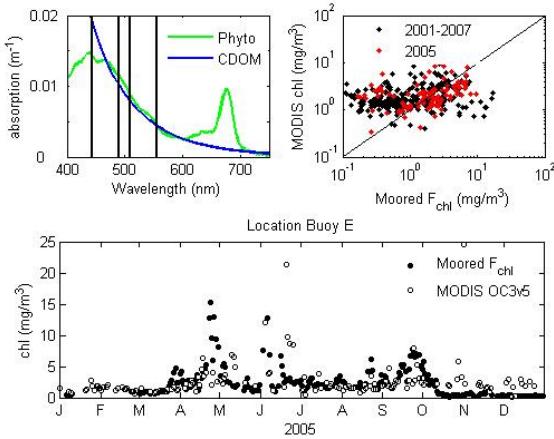


Figure 9. A. Phytoplankton and CDOM absorption with OC4v4 chl channels indicated, depicting similar absorption ratios. **B.** Daily MODIS OC3v5 chl vs. chl derived from calibrated chl fluorescence observations at Buoy E. Note MODIS estimates are rarely less than 2 mg/m³ due to residual CDOM contamination. **C.** Annual cycle in MODIS and Buoy E estimated chl for 2005 shows MODIS overestimation, particularly during periods of low chl periods and/or high river discharge of DOM.

IMPACT/APPLICATIONS

It is apparent that the impact of the Penobscot River on coastal waters is significant from the perspective of both biogeochemistry and optics. What is encouraging is that optical proxies appear to be robust to estimate the important biogeochemical parameters including the concentrations of phytoplankton, non-algal particles, CDOM and their associated carbon concentration. Additionally, optical proxies for compositional characteristics are also robust. Finally, the export of materials can be modeled from easily monitored optical, hydrological and hydrographic properties. This suggests that forecasting is also probable. Finally, we have begun to correlate certain components with land use in the sub-basins, which can be traced out of the river and estuary and into the coastal waters. This suggests that offshore monitoring might be sufficient to identify terrestrial land use changes.

RELATED PROJECTS

Both C. Roesler and A. Barnard are Co-PIs on a NASA sponsored multi-investigator research project examining the variability in fluxes of dissolved and particulate organic carbon from terrestrial sources to the Gulf of Maine via major rivers, and their subsequent fate within the Gulf of Maine. This work is specifically focusing on the impacts of riverine dissolved and particulate loading to the carbon cycle of coastal and offshore systems. Our ONR project is highly complementary to this project, as it is providing a better understanding of the variability in the concentration and composition of the Penobscot River dissolved and particulate materials and its subsequent delivery to the coastal and offshore regions, with the emphasis on optical properties rather than carbon properties.

The Gulf of Maine Ocean Observing System (GoMOOS; data to be found at <http://gyre.umeoce.maine.edu/buoyhome.php>), which Dr. Roesler is funded by to maintain optical instrumentation and data streams from the mooring observation program, is providing valuable hourly time series of coastal optical and physical surface properties upstream and downstream of the Penobscot River. Beginning in the fall of 2004, optical sensors (backscattering, chlorophyll and CDOM fluorometers) were installed on a GoMOOS mooring in the center of the mouth of the western branch of Penobscot Bay. Data from these systems are providing a wealth of information as to the hourly to seasonal variability in the dissolved and particulate materials within the river to coastal

transition zone of the Penobscot Bay. Additionally, CDOM fluorometers were added to the complement of sensors (ac9s, vsf, Ed and Lu) existing on the coastal shelf moorings upstream and downstream of Penobscot Bay.

(include web links as appropriate/available).

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